

Anisotropy of the segment mobility versus self-and pair-Correlation functions in polymer melts under mesoscopic confinement

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Abstract

Techniques typically used for studies of polymer dynamics such as NMR relaxometry, quasielastic neutron scattering, multiple-quantum build-up NMR, dielectric relaxation spectroscopy, and mechanical relaxation are specified and commonly classified in terms of correlation functions. Two categories of correlation functions are identified with respect to their specific ability to describe translational fluctuations on the one hand, and molecular reorientations on the other. The first category is of the dynamic-structure factor type reflecting the absolute or relative displacement behavior of particles. This type of function is in contrast to the second category, namely correlation functions of spherical harmonics of different orders characterizing rotational diffusion of molecules or molecular groups. In polymers, rotational diffusion tends to be strongly anisotropic. It is elucidated that the long-time tail of the correlation decay is particularly indicative for model characteristic features. The representation of experimental results by correlation functions instead of method-specific technical terms permits unambiguous comparisons and interpretations based on different techniques. This is demonstrated in the context of a problem of particularly topical interest, namely polymer melts confined in nanoscopic porous matrices. Methods probing correlation functions of spherical harmonics are shown to be sensitive to rotational chain dynamics severely modified under geometrical confinement, the so-called corset effect. On the other hand, correlation functions of the dynamical structure factor type characterizing translational fluctuations reveal little influence of such constraints in the experimentally accessible time/space window. In order to support this classification, the potentially competitive influence of wall adsorption effects is discussed in addition. Criteria permitting to rule out this sort of retardation mechanism under appropriate conditions are specified. © 2010 American Chemical Society.

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